Chapter 54 - **SOLVATION IN MIXED SOLVENTS**

1. SOLVATION OF MACROMOLECULES

Solvent interaction with macromolecules determines the miscibility characteristics and chain conformations. Macromolecules dissolve in good solvents, precipitate in poor solvents and cluster or aggregate in marginal solvents. Clustering characterizes water-soluble macromolecules. SANS measures both the clustering component at low-Q as well as the solvation component at high-Q. A typical SANS spectrum is shown from 4 % PEO/d-water.

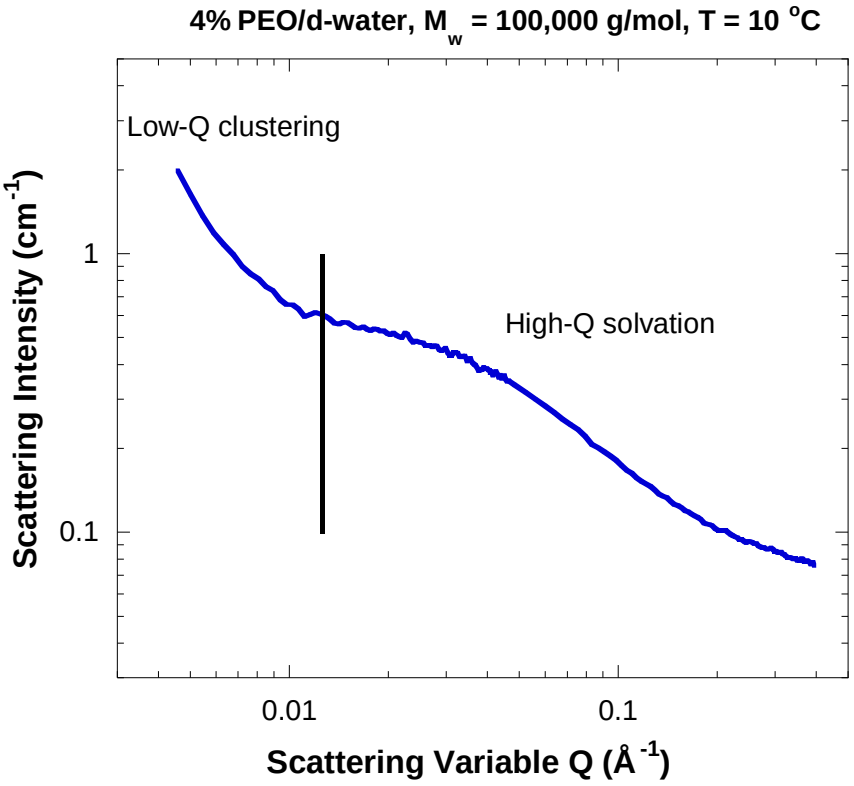

Figure 1: SANS data from 4 % PEO/d-water.

The low-Q and high-Q features are separated through a fit to the following empirical functional form.

$$I(Q) = \frac{A}{Q^n} + \frac{C}{1+(Q\xi)^m} + B \qquad (1)$$

The first term (power law) describes Porod scattering from clusters and the second term describes scattering from solvated polymer chains. B represents a constant incoherent scattering background. The solvation part is of interest here; parameter C is referred to as

the solvation intensity. Non-solvation would have been a better name for this parameter since C decreases when solvation gets better.

2. POLY(ETHYLENE OXIDE) IN WATER/ETHANOL SOLVENT MIXTURES

PEO/d-water solution is characterized by an LCST phase separation behavior (it phase-separates upon heating) whereas PEO/d-ethanol solution is characterized by a UCST phase separation behavior (it phase separate upon cooling). Note that PEO crystallizes in d-ethanol at low temperatures and that the UCST behavior is observed at high temperatures. Here, the solvation behavior of PEO in d-water/d-ethanol mixed solvent is described.

When the d-water fraction is increased, the solvation intensity (parameter C) is characterized by a minimum. It decreases then increases. This is the signature of non-ideal mixing behavior. Solvent molecules are not randomly mixed around the polymer chain. SANS cannot resolve the local cage-like structure formed by the solvent molecules, but it shows that the mixed solvents are more effective solvating agents than any of the individual solvents.

The solvation intensity is seen to decrease with increasing temperature at low d-water fractions (signature of UCST behavior) but increases with increasing temperature at high d-water fractions (signature of LCST behavior).

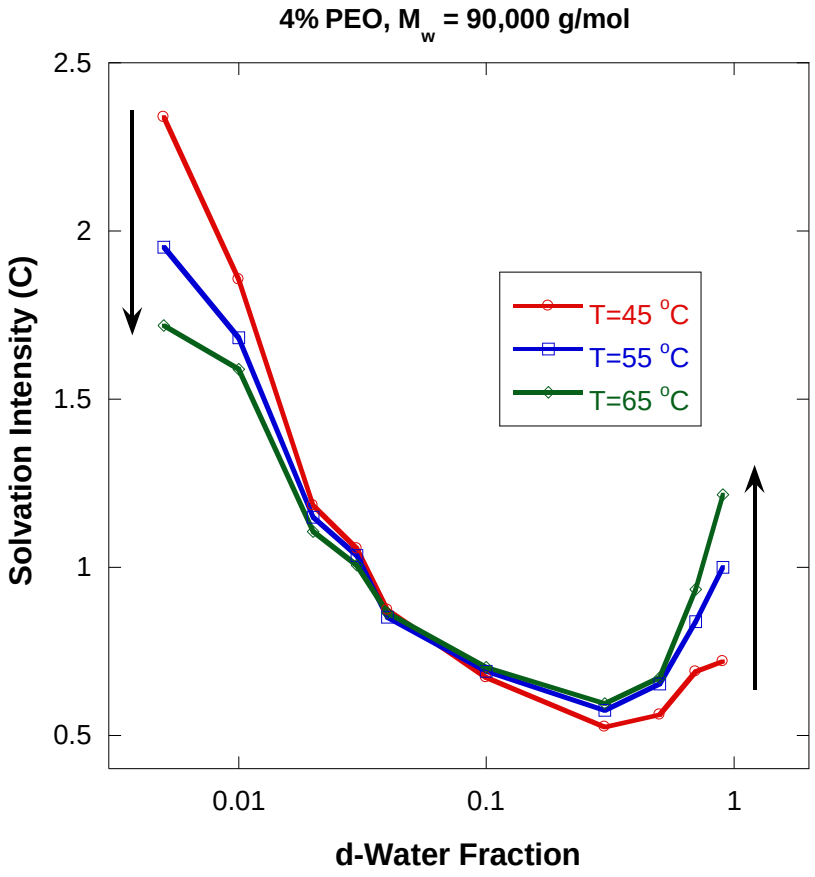

Figure 2: Variation of the solvation intensity (parameter C) with increasing d-water fraction (in d-water/d-ethanol mixtures) for three temperatures.

Variation of 1/C with 1/T yields an estimate of the spinodal phase separation temperature through the familiar extrapolation procedure. With increasing d-water fraction, the spinodal temperature is seen to decrease, disappear at low temperatures then reappear at high temperatures.

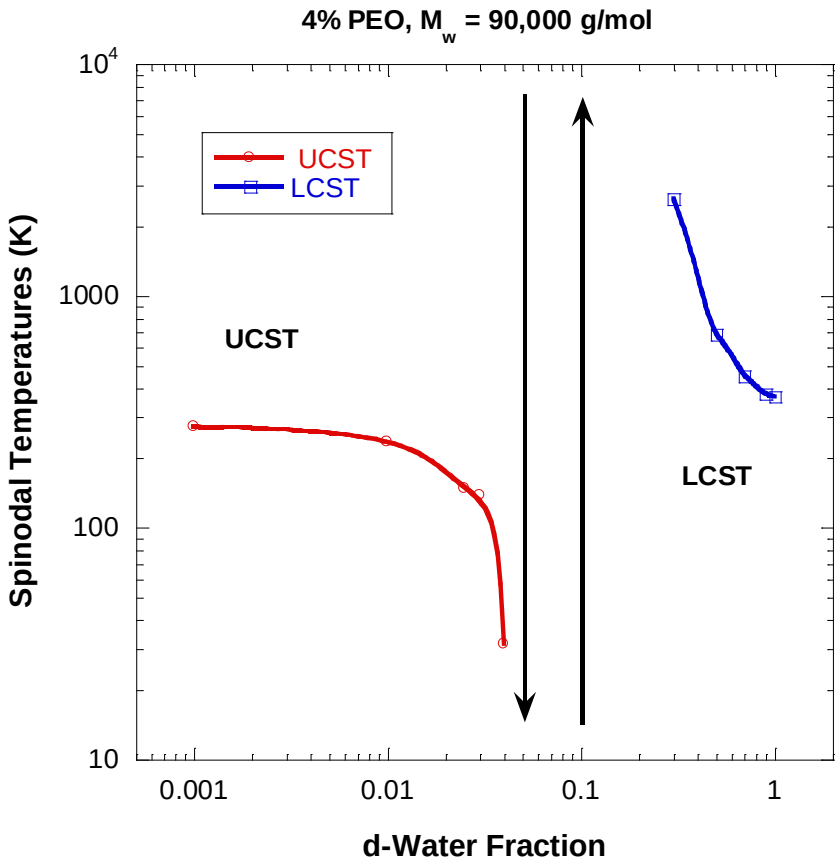

Figure 3: Variation of the spinodal phase separation temperature with increasing d-water fraction (in d-water/d-ethanol mixtures). Estimated spinodal temperatures were obtained through extrapolation.

Similar SANS measurements were made for PEO in other mixed solvent pairs in which d-water is one of the solvents. The same non-ideal mixing trend was observed in d-water/d-methanol and d-water/d-ethylene glycol (Hammouda, 2006).

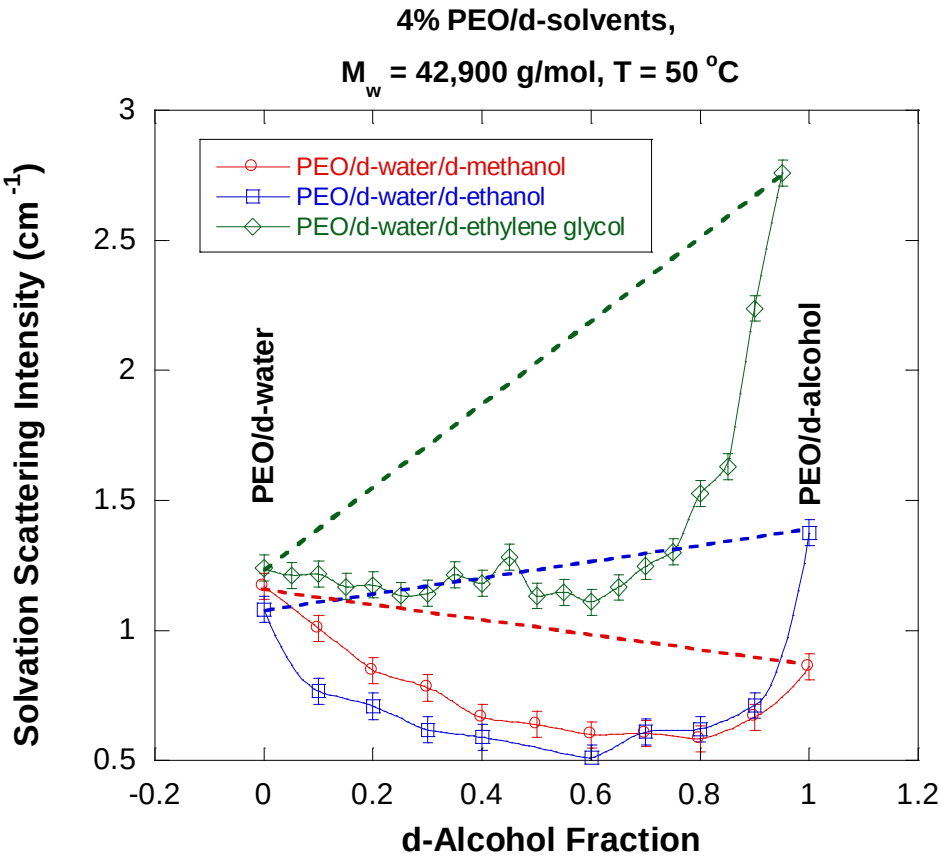

Figure 4: Variation of the solvation intensity with increasing d-alcohol fraction.

3. PEO/D-WATER/D-METHANOL TERNARY MIXTURES

PEO/d-methanol solutions are also characterized by crystalline behavior for low temperatures. In order to avoid PEO crystallization, SANS data at the elevated temperature of 50 °C are discussed here. To analyze the SANS data from PEO in mixed (d-water/d-methanol) solvents, the ternary Random Phase Approximation (RPA) model is used. This mean-field model is highly approximate for polymer solutions. The ternary RPA equations are not reproduced here. The three components are chosen as: A = PEO, B = d-methanol and C = d-water.

The degrees of polymerization and specific volumes are:

$n_A = 975$, $n_B = n_C = 1$
$v_A N_{av} = 38.94$ cm^3/mol, $v_B N_{av} = 40.54$ cm^3/mol, $v_C N_{av} = 18.07$ cm^3/mol,

Note that Avogadro's number ($N_{av} = 6.02*10^{23}$ /mol) was used to multiply the specific volumes. The scattering lengths are:

$b_A = 4.1326*10^{-13}$ cm, $b_B = 3.9133*10^{-12}$ cm, $b_C = 1.9145*10^{-12}$ cm.

The volume fractions for the three components are defined as ϕ_A, ϕ_B and ϕ_C. The two limiting cases of binary mixtures 4 % PEO/d-water and 4 % PEO/d-methanol (at T = 50 ^oC) are considered first. For the case of 100 % d-water ($\phi_B = 0$), the fit to the SANS data gives for the solvation intensity C = 1.171 cm^{-1}. This gives a Flory-Huggins interaction parameter of $\chi_{AC}/V_0 = \chi_{PEO/d\text{-}water}/v_0 = 0.0106$ mol/cm^3. For the case of 100 % d-methanol ($\phi_C = 0$), the fit to the SANS data gives C = 0.860 cm^{-1} which yields $\chi_{AB}/v_0 = \chi_{PEO/d\text{-}methanol}/v_0 = 0.0268$ mol/cm^3. The third Flory-Huggins interaction parameter χ_{BC}/V_0 is obtained (for example) from the case of 4 % PEO in 40 % d-methanol/60 % d-water solvent ($\phi_A = 0.04$, $\phi_B = 0.96*0.4 = 0.384$, $\phi_C = 0.96*0.6 = 0.576$). For this case C = 0.6648 cm^{-1} which yields $\chi_{BC}/V_0 = \chi_{d\text{-}methanol/d\text{-}water}/v_0 = 0.0099$ mol/cm^3.

This exercise shows that even-though it is highly approximate, the mean-field RPA approach provides a model for fitting SANS data from polymers in mixed-solvents.

4. DNA SOLVATION IN MIXED SOLVENTS

Salmon DNA undergoes a helix-to-coil transition in d-water at 94 ^oC and in d-ethylene glycol at 38 ^oC for 4 % DNA volume fraction and with the addition of 0.1 M NaCl. In order to investigate solvation in mixed solvents, SANS data were taken from DNA (same conditions) in d-water/d-ethylene glycol mixed solvents. Variation of the solvation intensity C with increasing d-ethylene glycol fraction at three temperatures (25 ^oC, 50 ^oC and 75 ^oC) shows clearly the helix phase and the coil phase (Hammouda-Worcester, 2007).

Note that the helix phase is characterized by ideal solvent mixing around the DNA phosphate groups whereas the coil phase is characterized by non-ideal solvent mixing just as for the PEO solution case.

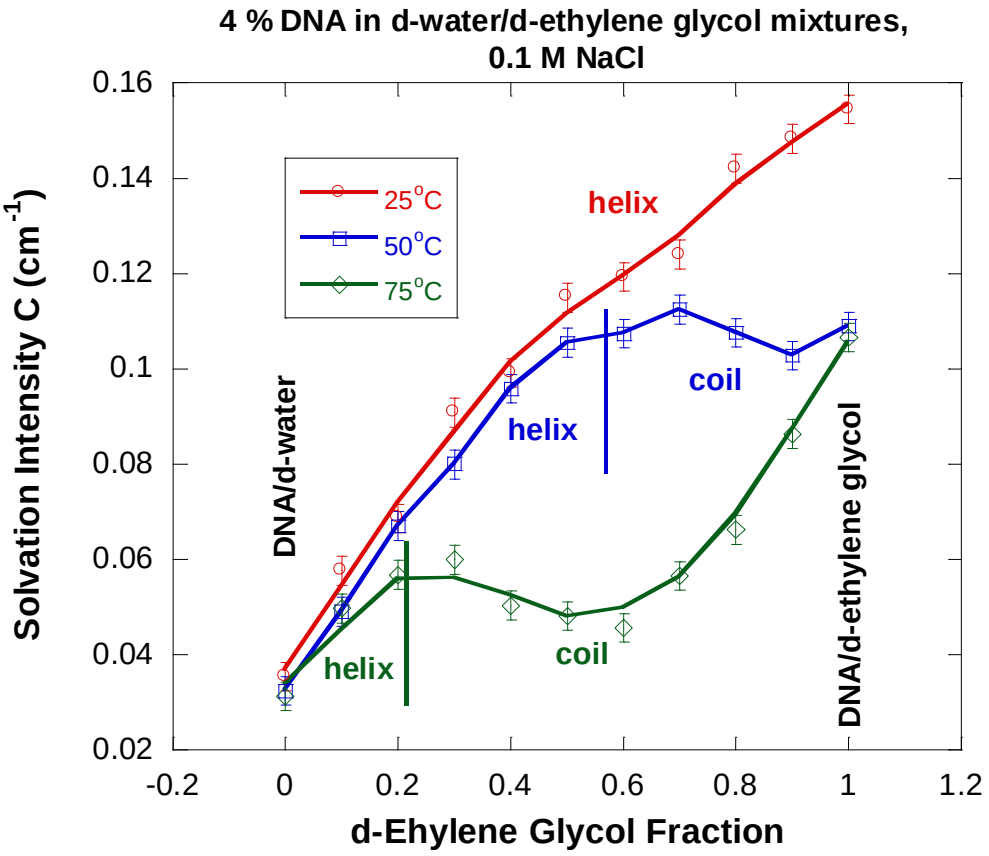

Figure 5: Variation of the SANS solvation intensity with increasing d-ethylene glycol fraction for DNA in d-water/d-ethylene glycol solvent mixtures shown for three temperatures.

REFERENCES

B. Hammouda, "Solvation Characteristics of a Model Water-Soluble Polymer", J. Polymer Science, Polymer Phys. Ed. 44, 3195-3199 (2006)

B. Hammouda and DL Worcester, "The Denaturation Transition of DNA in Mixed Solvents", Biophysical Journal 91, 2237-2242 (2006)

QUESTIONS

1. Is a PEO/d-water solution characterized by a Lower Critical Solution Temperature or an Upper Critical Solution Temperature? How about a PEO/d-ethanol solution?
2. What are the two main characteristic features of SANS data from water-soluble macromolecules?
3. How can one tell whether two solvents are mixed randomly or not around macromolecules?

4. Why is the DNA helix phase characterized by ideal solvent mixing?
5. Most polymers tend to dissolve better in solvent mixtures than in individual solvents. Name an exception to this.

ANSWERS

1. A PEO/d-water solution is characterized by a Lower Critical Solution Temperature; i.e., it phase separates upon heating. On the other hand, a PEO/d-ethanol solution is characterized by an Upper Critical Solution Temperature; i.e., it phase separates upon cooling.
2. SANS data from water-soluble macromolecules are characterized by a low-Q clustering feature and a high-Q solvation feature.
3. Two solvents are mixed randomly if the solvation intensity varies linearly between the two single solvent limits. Non-ideal mixing is characterized by nonlinear variation.
4. The DNA helix phase is characterized by random (ideal) solvent mixing because only the phosphate groups are in contact with the solvent. Different solvents interact similarly with the phosphate groups. The other groups (sugars and amine bases) are not in direct contact with the solvent.
5. Poly(N-isopropyl acrylamide) also referred to as PNIPAM does not dissolve in water and in solvents like methanol, ethanol or THF, but dissolves fine in mixtures of such solvents with water.